Proceedings of the XI International Seminar on
Mineral Processing Technology (MPT-2010)
Editors: R. Singh, A. Das, P.K. Banerjee, K.K. Bhattacharyya and N.G. Goswami
© NML Jamshedpur, pp. 247–254

RECOVERING IRON VALUES FROM IRON ORE SLIMES USING CATIONIC AND ANIONIC COLLECTORS

John Samuel Thella, Asim Kumar Mukherjee and Y. Rajshekar[1]
Research Development & Technology, Tata Steel Limited, Jamshedpur-831001, India
[1]RMIMTG, Tata Steel Limited

ABSTRACT

Indian iron ore industry is one of the world's largest and growing at a rapid pace. Approximately 15% of the plant input is discarded as slime into slime ponds. Slime dams are now considered as threat, due to lack of high grade ores and acute shortage of land. More over this slime also poses threat to the environment. In addition to the economic benefit from the utilization of the waste as a resource; it also minimizes the land requirement, surface degradation, groundwater pollution, and destruction of forests. Iron ore beneficiation plants in India gives in three products, coarse ore lumps, which are directly charged to blast furnace, the classifier fines with or without beneficiation are fed to sinter plants and the slime which contain high alumina and low Fe currently discarded as waste. Slimes are to be further beneficiated to produce concentrates low in alumina and silica. These slime which after pelletization can be used as burden for the blast furnace. In order to utilize iron ore slime an efficient gangue removal flotation process is indispensable. This research work presents the flotation route for the removal of gangue in the slime to a level which is acceptable for the blast furnace route production of iron. Research has been carried out effectively and efficiently to utilize iron ore slime from the slime ponds of Joda and Noamundi region, India. This research work presents the results on the application of flotation to obtain the hematite and goethite concentrate with low gangue content from iron ore slimes. Fine particle size, complex mineralogy and presence of locked particles make it impossible for direct production of hematite concentrate by froth flotation unless mineral surface specific collectors are used. With flotation of silicates by using cationic collector and starch as a depressant for iron ore, starch adsorption occurred on quartz particles covered by iron oxides and on minerals which contain, Fe (II), Fe (III), and Al ions in their structure. An entire flotation of mineral complex is possible if the collectors used are mineral surface specific. Flotation performance was optimized by carrying out design of experiments.

Keywords: *Iron ore Slimes, Flotation.*

INTRODUCTION

In order to effectively utilize iron ore slime, research was oriented towards technology development for slime beneficiation. The goal of this research work is to investigate possibilities for development of an effective and profitable technology through flotation to obtain hematite concentrates with high Fe content and low alumina and silica content. The technique of selective separation by froth flotation can effectively be applied only to those mixtures in which the particles to be separated are present as liberated grains. To become levitated by the buoyancy of the bubble, these particles must be smaller than a maximum size. The maximum size is generally

below 300 Microns, and the limiting parameter is the adhesion between the particle and the bubble. Flotation becomes less effective when the particle size is below 10 Microns. But on the other hand metallic ions and colloidal-size precipitates are readily floated, so their behavior in effect signifies that no lower limit of particle size exists. If the solid phase to be floated is not fully liberated from other solid phases in the mixture, the resultant composite particles can still be floated, but the separation is not as absolutely selective as it should be, since the float product is unavoidably contaminated with the adjoining solid components. In iron ore flotation we are dealing with oxide systems and knowledge of the condition of the mineral surfaces is essential to an understanding of the flotation process. Both silica and iron oxides acquire a surface charge in aqueous environments through acquisition of hydroxide or hydronium ions at the fractured bond sites, with the sign and magnitude of the charge being dependent on the pH of the system. For example, at about pH 2, silica is electro neutral; at a lower pH, silica surfaces exhibit a net positive charge, and above pH 2, the silica surface carries a net negative charge. Similarly, iron oxides accumulate a net excess of either positive or negative surface charges, with the obtained condition again being dependent on the pH. A pH of about 7 is usually reported as the point at which electro neutrality occurs at the various iron oxide surfaces. The fact that the mineral surfaces are subject to a varying surface charge influences the pH at which flotation is performed through the choice of the collector. Anionic collectors are the logical choice when the pH of the system is such that the mineral to be collected bears a net positive charge; cationic collectors are selected when the opposite condition of surface charge prevails. However, it should also be noted that these observations pertain to an ideal system, and that in treating ores as opposed to pure minerals, actual conditions may produce a deviation from the expected behavior. Iron ore flotation is generally concerned with the separation of the iron oxide minerals from those containing gangue. For these ores the flotation method employed may be that which recovers iron minerals in the froth (direct flotation), or, alternatively, that by which the siliceous gangue is contained in the froth product (reverse flotation). The ore is slurried with water and conditioned with reagents to provide selectively coated hydrophobic surfaces on one of the mineral species. Upon introduction of air, these reagent-coated minerals attach themselves to air bubbles, rise to the surface, and are subsequently removed from the system. The reagent suite employed may be simple or complex.

Because collectors are the most important reagents in any flotation system, it is worthwhile to list some of their properties and other desirable features. The two main classes of iron ore collectors are as follows: (a) Anionic: Organic acids containing a hydrocarbon group, and/or the ammonium, potassium, or sodium salts of these acids. In iron ore flotation the important reagents in this group would include the straight chain fatty acids and soaps. (b) Cationic: Organic bases containing a hydrocarbon group, and the salts of these bases, usually chlorides or acetates. This group includes the primary aliphatic amines, diamines, quaternary ammonium salts and ether amine products. These reagents are generally used to float siliceous minerals. Cationic collectors find their greatest utility in flotation of the siliceous constituents.

EXPERIMENTAL

Materials

Reverse cationic flotation was carried out to float silica and alumina gangue using amine based cationic collector. Potato starch was used as a depressant for iron bearing minerals. Sodium hydroxide was used as a pH regulator. In direct flotation fatty acid as collector and pine oil as frother was used.

Size wise chemical analysis of iron ore slime from Joda, India is presented in Table 1. From the Table 1, D_{50} of the slime is around 25-20 microns, which is very fine. Around 50% of the slimes are present in <25 Micron fractions having 58.28 % Fe and 4.76% SiO_2 and 3.43% Al_2O_3.

Table 1: Size wise chemical analysis of Joda iron ore slimes

Micron	Wt%	Fe(T)	SiO_2%	Al_2O_3%
100	10.87	54.11	7.32	4.61
–100+50	9.53	59.50	3.93	3.52
–50+37	15.67	53.31	5.09	4.44
–37+25	11.96	60.88	3.78	3.01
–25	51.97	59.83	4.51	2.96
Total	100	58.28	4.76	3.43

Methods

Flotation test were performed in a 2.5 liter Denver flotation cell. Feed of 20% solids and airflow rate of 2 LPM were maintained. Amines are used as a collector in reverse cationic flotation, and starch as depressant for iron bearing minerals. Fatty acid is used as a collector in direct flotation. pH is regulated by using sodium hydroxide. Conditioning time of 5 minutes for starch, 15 minutes for collector, and 3 minutes for frother was maintained through out the test. Froth was collected for 3 minutes. Concentrate and tailings were chemically analyzed.

RESULTS AND DISCUSSION

Mineral mapping and modal mineralogy of flotation feed

Back Scattered Electron (BSE) imaging technique was used for identifying the phases and EDS coupled with SEM was used for microanalysis of the different phases. Total iron, aluminum, silicon and, phosphorus content were analyzed for each phases. Hematite and goethite was identified as the major iron bearing mineral phases. Kaolin, gibbsite and, quartz are other minerals present as gangue phase in the slime.

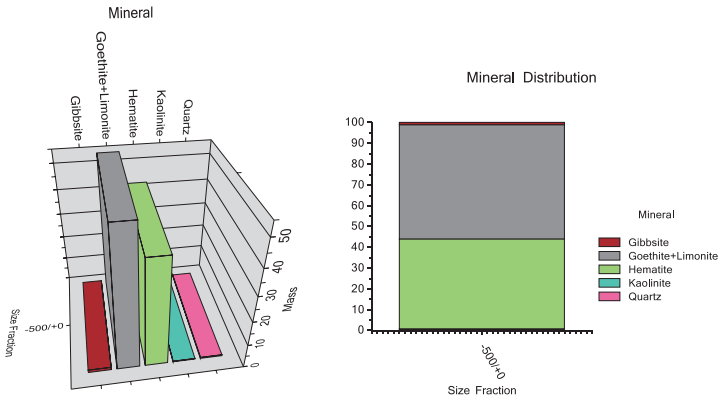

Fig. 1: Modal mineralogy of flotation feed.

Fig. 1 shows the modal mineralogy of flotation feed. Major iron bearing phases are hematite and goethite and gangue bearing minerals are quartz, kaolinite and gibbsite. Goethite phase is around 50% which contains Al and Si distributed inside the matrix. Goethite (FeOOH), a common mineral in iron ores, is formed during chemical weathering of iron ores and banded iron formation. It contains variable amounts of other elements such as Al, Mn, P, Si. etc. in crystal structure. Aluminum ranks first among the various possible substitute in both natural and synthetic goethite. It has been stated that the basic structural unit of goethite is a distorted octahedron. In such a structure, Al3+ partly replaces the central Fe3+ cation. Fig 2 shows the association of different mineral phases, most of the gangue phases are associated with goethite phase.

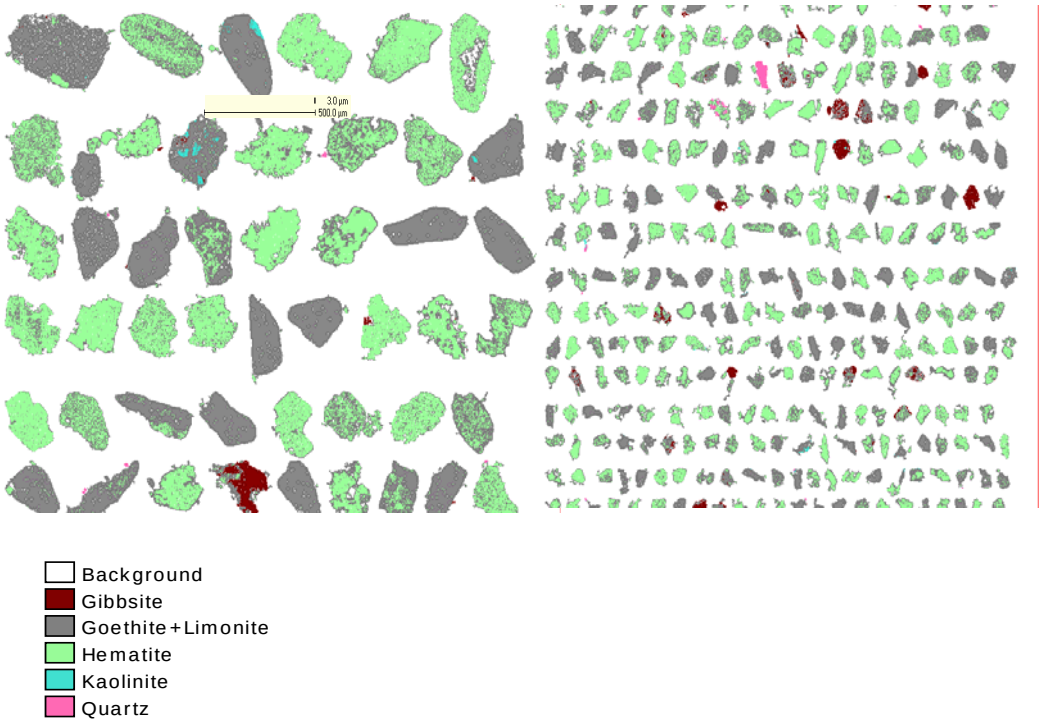

Fig. 2: Mineral mapping of flotation feed.

Reverse cationic flotation with amines

Two stage flotation with amines was carried out. In stage I, collector dosing of 1 Kg/T of amine and 0.2 Kg/T of starch as a depressant for iron bearing minerals is maintained. The concentrate from the stage I is again floated with 0.5 Kg/T of amine II which is a powerful alumina and silica collector. Sodium hydroxide is used as a pH regulator. pH of 9.5 is maintained throughout the experiment.

The result obtained is 64.5% Fe, 2.18% Al_2O_3 and 1.69% SiO_2 with a yield of 27.32% and Fe recovery of 28.74% The results are shown in Table 2. Individual assays of stage I and stage II tailings and final concentrate is presented in Table 3.

Table 2: Chemical assays of concentrate and tailings

Amine Collector	Concentrate	Tailings
Wt%	27.32	72.68
Fe%	64.5	60
Al_2O_3%	2.18	3.47
SiO_2%	1.69	5.07
Fe Recovery	28.74	71.26

Table 3: Individual assays for Stage I and Stage II

	Wt%	Fe%	Al_2O_3%	SiO_2%
Concentrate	27.32	64.5	2.18	1.69
Tailing I	26.72	56.42	3.87	10.96
Tailing II	45.96	62.2	3.24	1.66

Table 4: Percentage distribution of Al and Si in concentrate and Tailings of stage I and Stage II

	Stage I		Stage II	
	%Al D	%Si D	%Al D	%Si D
Concentrate	67.38	28.71	19.56	10.07
Tailings	32.62	71.29	80.44	89.93
Head	100	100	100	100

Stage I is having highest selectivity index of 1.70 as compared to stage II selectivity index of 0.77, because of the less percentage distribution of Fe in stage-1 tailings as compared to stage-II tailings, It is evident that amine II is powerful collector for alumina and silica than amine I from the percentage distribution values of 19.56% alumina and 10.07% silica in stage II concentrate compared with 67.38% alumina and 28.71% silica in stage I concentrate.

With increase in collector dosing from 0.5 to 2.5 Kg/T there is a gradual decrease in percent alumina in the concentrate. Silica levels in the concentrate increased with 0.75–1.0 Kg/T collector, and then gradually decreased upto 2 Kg/T collector. This is explained as follows, up to 1.0 Kg/T collector the dosing is sufficient to form a monolayer on alumina particles and silica particles are less coated, with increase in dosing from 1.0Kg/T to 2 Kg/T the collector dosing is sufficient enough to form a layer on alumina and silica particles, hence alumina along with silica bearing particles reported to the froth.

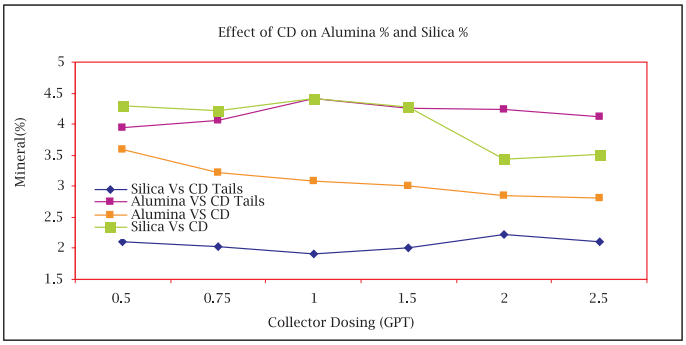

Fig. 3: Effect of collector dosing on alumina percent and silica percent with amine collector.

Fig. 3 shows the effect of collector dosing on alumina percent and silica percent.

Anionic flotation with fatty acid collector

Flotation experiments are carried out with a collector dosing of 2 Kg/T. Twenty percent solid in the feed slurry, airflow rate of 2.5 liters per minute and stirrer speed of 1000 rpm is maintained. pH of 9.5 is maintained with sodium hydroxide. Pine oil is used as a frother. The results obtained are shown in Table 5.

Table 5: Chemical assays of concentrate and tailings with fatty acid collector

	Wt%	Fe_2O_3 %	Al_2O_3%	SiO_2%	FeD	AlD	SiD
Conc	55.66	62.9	2.69	2.94	57.85	46.11	38.09
Tails	44.34	59.16	3.9	5.98	42.85	53.89	61.91

Concentrate having 62.9% Fe, 2.69% Al_2O_3 and 2.94 % SiO_2 with an yield of 55.66% is obtained with Fe recovery of 57.85%.

Two stage combination of reverse and cationic flotation

Two stage flotation experiments are carried out. In stage-I reverse cationic flotation with amine using SHMP as dispersant and starch as depressant. In stage-II, concentrate from stage-I is further subjected to direct flotation with fatty acid. The results are shown in Table 6. Concentrate having 62% Fe, 2.65% Al_2O_3 and 2.48 % SiO_2 with an yield of 33.3% is obtained with an Fe recovery of 34.36%.

Table 6: Chemical assays of concentrate and tailings—Reverse flotation in stage I and Direct flotation in stage II

Index	Concentrate	Tailings
Wt%	33.3	66.7
Fe%	62	58.93
Al_2O_3%	2.65	3.7
SiO_2%	2.48	5.09
Fe Recovery	34.36	65.64

Optimum results obtained with cationic flotation and anionic flotation is shown in Fig. 4.

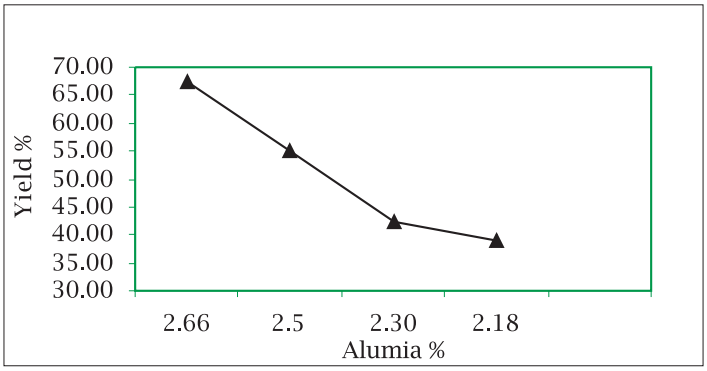

Fig. 4: Optimum results–Percent Alumina versus percent yield

Experiment	Conditions	Alumina %	Yield %
A	Reverse Cationic Flotation	2.66	67.51
B	Direct Flotation Mixed Product	2.50	55.00
C	Direct Flotation with Fatty acid, Frother 0.1 Kg/T, 3 mins FCT	2.30	42.17
D	Direct Flotation with Fatty acid, Frother 0.15 Kg/T	2.18	38.9

CONCLUSIONS

From the characterization studies the feed material is highly complex with poor liberation and the gangue minerals are still intimately associated with iron bearing minerals. Efficient recovery of iron values with low alumina and silica requires proper liberation. Grinding the material to a finer degree is not economical as the material is already very fine. After carrying out different methodologies employing different mineral surface specific flotation reagents, the optimum results found are, iron concentrate of 63% Fe and 2.3% alumina with an yield of 42.17% is achieved. The optimum conditions for the anionic flotation with fatty acid is 9.5 pH and 4 Kg/T of collector dosage. It was found from design of experiments that collector concentration and pH plays vital role in flotation performance.

ACKNOWLEDGEMENTS

Authors wish to acknowledge Prof. Zhong Hong, school of chemistry and chemical engineering, Central South University, Changsha, China, for his valuable suggestions in developing mineral surface specific collectors, Dr. D.K. Sengupta, Ex-Scientist, RRL-Bhubhaneswar for his technical guidance. Dr. Tamal K. Ghosh for characterizing the feed samples, Dr. Pradip Kumar Banerjee for his periodic suggestions and co-operation during the course of research work.

REFERENCES

[1] Peres, A.E.C. and Correa, M. I., 1996, Depression of iron oxides with corn starches, *Minerals Engineering*, **9(12)**, p. 1227.

[2] Mukherjee, A.K., 2009, A new method for evaluation of gravity separation processes, *Mineral processing and Extractive metallurgy Review*, **30**, p. 191.

[3] Vieira, Ana M. and Peres, Antonio E.C., 2007, The effect of amine type, pH, and size range in the flotation of quartz, *Minerals Engineering*, **20**, p. 1008.

[4] Shergold, H.L. and Kitchener, J.A., 1975, A surface chemical study of adsorption of flotation collectors on a Swedish hematite, *International Journal of Mineral Processing,* **2**, p. 249.

[5] Dogu, I. and Arol, A.I., 2004, Separation of dark-colored minerals from feldspar by selective flocculation using starch, *Powder Technology,* **139**, p. 258.

[6] Laskowski, J.S. and Nyamekye, G.A., 1994, Colloid chemistry of weak electrolyte collectors: the effect of conditioning on flotation with fatty acids, *International Journal of Mineral Processing*, **40**, p. 245.

[7] Leja, J., 1982, Surface Chemistry of Froth Flotation.

[8] Morgan, Leslie J., Ananthapadmanabhan, K.P. and Somasundaran, P., 1986, Oleate adsorption on hematite: Problems and methods, *International Journal of Mineral Processing,* **18**, p. 139.

[9] Filippov, L.O., Filippova, I.V. and Severov, V.V., The use of collectors mixture in the reverse cationic flotation of magnetite ore: The role of Fe-bearing silicates, *Minerals Engineering* 23 (2010) 91–98.

[10] Pearse, M.J., 2005, An overview of the use of chemical reagents in mineral processing, *Minerals Engineering*, **18**, p. 139.

[11] Pearse, M.J., 2003, Historical use and future development of chemicals for solid–liquid separation in the mineral processing industry, *Minerals Engineering,* **16**, p. 103.

[12] Pearse, M.J., Weir, S., Adkins, S.J. and Moody, G.M., 2001, Advances in mineral flocculation, *Mineral's Engineering,* **14**, No. 11, p. 1505.

[13] Pradip, Beena Rai, 2003, Molecular modeling and rational design of flotation reagents, *Internation J. Miner. Process,* **72**, p. 95.

[14] Zhong, H., Liu, G.Y., Xia, L.Y., Lu, Y.P., Hu, Y.H., Zhao, S.G. and Yu, X.Y., 2008, Flotation separation of diaspore from kaolinite, pyrophyllite and illite using three cationic collectors. Miner. Eng., **21**, p. 1055.